As a result of the quantum effects, nanoparticles (NPs) often exhibit novel properties that differ enormously from that of their bulk materials.[1] Notably, NPs packed in 2-dimensional (2-D) or 3-dimensional (3-D) arrays often possess unique electrical,[2, 3] optical,[4, 5] and magnetic[6] properties that stem from both the properties of the individual particles and the electron coupling between neighboring particles.[7, 8] 2-D NP arrays have been particularly closely studied, most often as deposited layers sitting on planar solid supports which are either adsorbed from solution or deposited as a colloidal suspension dried onto the surface.[9-12]

An elegant method of obtaining NP 2-D arrays is through spontaneous self-assembly at liquid-liquid interfaces to form metal liquid-like films (MeLLFs). These are densely packed monolayer metal NPs self-assembled at the interface between two immiscible liquids, which can be obtained simply by shaking a non-water-miscible organic solvent with a portion of aqueous metal colloid in the presence of a low concentration of a chemical compound (a “promoter” or “modifier”) which promotes particle adsorption at the interface.[13-19] These mobile arrays have the same characteristics as the best of the deposited NP films in that they are densely-packed, electronically coupled monolayers of particles which can readily be prepared on the cm² scale at room temperature in minutes with no specialist equipment.

Although these MeLLFs have been known for many years they have not been widely
exploited because the particles are difficult to access since they sit between two liquid layers. There have been some attempts to develop methods to transferring them from liquid phase into freestanding films. Several research groups have shown that by drying MeLLFs over holey substrates micrometer-sized freestanding arrays can be created.\textsuperscript{20-22} To transform MeLLFs into larger freestanding cm\textsuperscript{2} scale films, up to now the most effective approach was to sinter the particles but this gave a final product which was too weak even to withstand direct characterization under electron microscopy.\textsuperscript{23} The alternative approach of in-situ polymerization of monomers linked on the surface of NPs can transform MeLLFs into freestanding films.\textsuperscript{24} However, although these films are stronger than the sintered analogues, the NPs are completely trapped within an isolating polymer layer which removes most of their potential applications since it prevents both chemical interaction and physical contact with the NPs.

Ideally, what is required is a method to convert the mobile interfacial particle arrays into freestanding films which are strong enough for routine handling and device construction but still retain the structure of the MeLLFs and leave the particles chemically and physically accessible. This is much more challenging than simply encasing the particle arrays in polymer. Here we report a general and ‘one pot’ method to achieve all these goals by growing a supportive thin polymer film in-situ at the organic side of the MeLLF’s liquid/liquid interface. This approach means that the particles are fixed onto the surface of the supporting polymer films rather than sitting on top of them or being trapped within them, which is why we have named them SENS (Surface-Exposed Nanoparticle Sheets).
Scheme 1. Schematic illustration of the ‘one pot’ fabrication process of SENS. The mixture shown in (a) is shaken (b), to give a self-assembled NP monolayer sitting at the liquid-liquid interface (c). Evaporation of the dichloromethane (DCM) phase forms a robust and uniform layer of polymer support to hold the NPs together (c and d). Water is added (e) so the film floats free and can be lifted (f) to give the final SENS as shown in reflection and transmission (g).

**Scheme 1** illustrates the fabrication process: initially a mixture of metal colloid and a polystyrene/DCM solution were shaken vigorously in the presence of a promoter in a hydrophobic container to form a lustrous and mobile film of NPs at the liquid-liquid interface (Scheme 1(a) and (b)). The promoter, which consists of a hydrophilic cation, stabilizes the negatively charged NPs at the liquid/liquid interface by providing charge-screening.[16] A hydrophobic container was used so that the DCM wrapped around the aqueous layer, meaning that the MeLLF partly sat at the top surface of the liquid-liquid interface (Scheme 1(c)). Evaporation of the upper DCM layer caused the growth of a thin polystyrene film on the part of the NPs in the organic phase (Scheme 1(d)). To allow sufficient time for the metal films to
form at the interface before polymer deposition occurred, the rate of evaporation was decreased by covering the container with an inverted beaker. This also increased the uniformity of the resulting films over those prepared with an open vessel. After all the DCM had evaporated the upper surface of the film was broken away from the rest with a scalpel and floated to the top by adding excessive water. The film could then be lifted using a smooth flat scoop slid horizontally under the film (Scheme 1(e)). During the lifting process the scoop makes direct contact with the hydrophilic NPs so is best made from a hydrophobic material in order to prevent sticking.

The optical properties of the SENS are very similar to those of the parent MeLLFs, in particular the films retain their highly reflective metallic appearance (see Scheme 1g, Figure S1(a) and (c) for Au, Figure S2 for Ag). In addition, when viewed in transmission the Au films have the expected blue color (Figure S1(b)) as the parent MeLLFs. This color arises from strong intraparticle coupling which can be observed in the UV/vis extinction spectra of both the MeLLFs and SENS since it causes red-shifting and broadening of the unaggregated gold colloid’s plasmon peak at ca. 525 nm.

The SENS were sufficiently robust to be handled with tweezers and were flexible enough to be folded in half without snapping. Moreover, they were strong enough to withstand the 20 kV electron beam without damage during repeated scanning electron microscope (SEM) measurements and focused laser illumination in SERS analysis (see below).
Figure 2. SEM and Atomic force microscopy (AFM) of SENS. (a) SEM image of a cross-section of a typical SENS showing the particles localized at one face of the film. (b) Cross-section of the same film at higher magnification. (c) Tilted view of a damaged area of silver SENS showing particles anchored by sitting partly within the polymer support. Plan view of a typical section of silver SENS (d) and gold SENS (e) showing a field of densely packed NPs. SEM plan view (f) and AFM 2-D image (g) of gold SENS with a lower concentration of NPs. (h) Cross-section height profile along the black line drawn in (g). Scale bars in all images represent 1 µm.
Electron microscopy was used to characterize the microstructure of the SENS. Figure 2(a) shows a cross-section of a typical SENS in which the polymer layer is ca. 2.5 µm thick. The particles are localized at a single face, as illustrated in Scheme 1(g). Figure 2(b), which is a higher magnification cross-section shows a monolayer of particles sitting at the top surface. The particles within this layer have the expected structure of a densely-packed monolayer as shown in the plan views (Figure 2 (d) and (e)). Figure 2(c) shows an image of a damaged area near the edge of the SENS which gives a clearer view of how the bottom of each of the NPs sit within the polymer support, anchoring them in place. This final structure is consistent with the observation that the particles in the SENS carry a citrate/and or chloride surface layer which makes them hydrophilic, so they will sit predominantly at the aqueous side of the liquid-liquid interface while the polymer is deposited from the organic side of the interface. Figure 2(f) show a gold SENS with a lower concentration of NPs ca. 25 nm in diameter to reveal the polymer backing. By conducting AFM topography measurements of the film it was shown that the monolayer of NPs were ca. half-way embedded into the polymer suggesting that the NPs had a near 90 ° contact angle at the interface (Figure 2(g) and (h)). This is consistent with the calculated profile of self-assembled NP monolayers at liquid-liquid interfaces. [17, 25]

Of course neither high magnification SEM or AFM would be able to detect if there was a thin (< 2 nm) layer of polymer covering the particles and such a problem is a real possibility. However, this can be tested using contact angle measurements and direct chemical reactivity tests. Figure 3 compares images of the equilibrium water contact angle of a pure polystyrene film with both sides of the SENS. As expected, the polymer face has an identical contact angle to the model polystyrene sample while the particle side is significantly more hydrophilic with a contact angle of 51.7 °, matching previous literature reports for contact angle between pure water and gold surfaces covered with organic surface species.[26] In addition, application of aqua regia to the particle side caused immediate loss of the reflective layer, leaving the
transparent polystyrene film (Figure S3). Conversely, application of the same acid to the polymer side had no effect on the films.

Figure 3. Contact angle measurements and acid droplet experiment. Contact angle between a pure polystyrene film and water (a), the polystyrene side of gold SENS and water (b), the NP side of gold SENS and water (c). (d) Optical image of a gold SENS holding a droplet of aqua regia on its polymer side.

All the observations above combine to confirm that the NPs are indeed only partly submerged into polymer, which holds them in place while still leaving the majority of their surfaces exposed. This is in sharp contrast with previous cases where the NPs were completely trapped inside polymer.[24] Conversely, the particle films are also different from materials where the particles sit on top of a substrate because here the particles are firmly fixed to the polymer backing, which makes them much more mechanically robust. In attempts to measure the scratch hardness of the films using the ASTM Pencil Test we found that with pencils harder than 5B the tips gouged the polystyrene films before any particle shedding was observed.[27] Similarly, the films can be submerged in agitated water for > 12 hours without any noticeable loss of particles.
The method is very general since SENS with different nanoparticles/supporting polymer can readily be prepared by changing the starting materials. Examples of SENS prepared with different metals and polymers (gold and silver on polystyrene and poly (methyl methacrylate)) are shown in Figure S4. Similarly, the film thickness can be changed by altering the amount of polymer added. In this work the films were typically prepared with 0.05- 0.08 g/mL of polystyrene in DCM to give ca. 2 µm films but concentrations from 0.02 to 0.12 g/mL were tested and gave films ranging from 0.5 – 10 µm. The size of the films can easily be changed by altering the size of the interfacial area. For convenience the films discussed above were typically prepared in 60 mm diameter containers which gave ca. 60 mm diameter circular SENS that could be cut to different sizes as required. However, the process is scalable so for illustration a sample with diameter of 150 mm was prepared and lifted out of the liquid after it was broken away from the sides of the container by adding water following the protocol shown in Scheme 1e (Figure 4a). Even in this simple laboratory demonstration, a ca. 170 cm² SENS could be produced.

Figure 4. Large scale fabrication of SENS and examples of applications. (a) Photograph of a silver SENS in-situ (top image). The scale bar on the picture represents 7 cm. The bottom
image shows the silver SENS being lifted from the water. (b) SERS spectrum of silver SENS with either the polymer side (1) or the NP side (2) exposed to vapor above a 10^4 mol/L thiophenol/water-ethanol solution. (c) Silver SENS catalyzed reduction of nitrophenol to aminophenol (right) compared with the uncatalyzed reaction (left). (d) Silver SENS applied as conducting material used to light a LED. (e) Colonies of Gram negative bacteria grown from inoculum drops placed in contact with simple polystyrene (1) and the NP side of a silver SENS (2), illustrating its antibacterial activity.

The combination of an easily accessible particle layer with straightforward scalable preparation means the SENS have considerable potential for application across a wide range of fields, some of which are illustrated here. MeLLFs have previously been shown to be excellent SERS enhancing media; the SENS retain this enhancement but provide it in a much more convenient solid film. [19] Figure 4(b) demonstrates head space detection of thiophenol above a dilute aqueous solution. Consistent with our proposed model, the original citrate/chloride surface species were retained on exposure of the polymer side to the vapor with barely detectable thiophenol bands while exposure of the particle side gave strong thiophenol spectra with an enhancement factor of ca. 6.0 × 10^7 (Figure S5).

Figure 4(c) shows a silver SENS used as a dip-in catalyst for the reduction of p-nitrophenol to p-aminophenol. The reaction was monitored using UV/Vis absorption spectroscopy (Figure. S6). In the absence of the SENS, the reactant peak at 401 nm remained unaltered after 24 h while addition of a 4 cm^2 SENS gave 95% reduction in 1 h.

The SENS show surprisingly high conductivity considering the parent MeLLFs have been reported to be non-conducting and the films are composed of thin layers discrete particles (Figure. 4d). [13, 14] The mean sheet resistance of silver SENS measured using a four point probe was ca. 53±18 Ω/□, which is comparable with the 75-80 Ω/□ value previously reported for highly conductive carbon nanotube/conducting polymer matrices. [28]
The silver particle sides of SENS show significant microbicidal activity. 20 µL droplets containing 10^7 cfu/mL gram-negative or gram-positive bacteria were placed onto the particle side of the SENS or the plain polystyrene control material. After 4 hours the SENS samples showed a 1 log reduction in CFU for the gram-positive and 2 log reduction for the gram-negative bacteria (Figure. 4e.)

The ability to prepare SENS with a wide range of components allows them to be optimized for each application. For example, the rate of nitrophenol reduction was significantly higher with silver SENS than gold SENS prepared with 10 ±1 nm gold NPs and much higher than that observed with large gold particles. Conversely gold SENS prepared with 35 ±10 nm irregularly shaped NPs had significantly higher conductivity than SENS prepared with spherical 10 ±1 nm gold NPs.

In summary, we have designed a surprisingly simple “bottom-up” method to prepare highly-organized nanostructured materials which combine the advantages of both the exposed films formed by solvent evaporation onto solid supports and freestanding flexible NP-embedded polymer matrices. The combination of room temperature self-assembly of NPs with solvent evaporation induced polymer growth gives this one-pot method scalability, simplicity and cost-efficiency vastly superior to previous methods of fabricating freestanding NP films. Since the SENS are planar 2-D assemblies of NPs they can be readily used for the applications already proposed for 2-D NP arrays such as sensors, plasmonic displays, dip-in catalysts etc. but at dramatically reduced cost. It has been shown that many interesting materials can be assembled at the liquid-liquid interface. However, an effective way to extract them for further characterization and applications is still lacking.\textsuperscript{[29, 30]} Here our method provides a potentials way to achieve this and in addition the active components in SENS can be post-processed because the particles remain accessible. This means that SENS can provide a general approach to creating generic components for a wide range of more complex engineered nanodevices.
Experimental Section

Materials: Silver nitrate (99.9999%), gold (III) chloride hydrate (99.9999%), trisodium citrate, tetrabutylammonium nitrate, p-nitrophenol, sodium borohydride, nitric acid (≥65%), thiophenol, DCM, poly (methyl methacrylate) (M. W. 15000), conductive copper tape and screw-cap polypropylene centrifuge tubes were purchased from Aldrich Ltd. Polystyrene (M. W. approximately 100000) was purchased from BDH chemicals Ltd. The chemicals were used without further purification. Water used throughout all experiments was low TOC (<3.0 ppb) 18.2 MΩcm water. For antibacterial tests, Pseudomonas aeruginosa PA01 and Staphylococcus aureus ATCC 6538 were obtained from LGC Standards, Middlesex, UK. Mueller-Hinton agar plates, phosphate-buffered saline, tryptone soya broth and quarter-strength Ringers solution were obtained from Oxoid Ltd, Basingstoke, UK.

Instrumentation: Extinction spectra were measured on an Agilent 8453 photodiode array UV-vis spectrophotometer in 1 cm quartz cuvettes with water or DCM references used as appropriate. SENS were referenced against air. Reduction of p-nitrophenol was monitored at room temperature (ca. 20 ºC). ca. 4 cm² SENS were used for all catalyzed reactions. Raman spectra of SENS were collected using a Perkin Elmer RamanMicro 200 Raman Microscope equipped with a 785 nm diode laser. In a typical contrast experiment, SERS spectrum of SENS were collected with either side of SENS exposed to 1.5 mL of 10⁻⁴ mol/L thiophenol/water-ethanol solution in an enclosed 35 mL bottle overnight. The two pieces of SENS were fixed to a piece of standard adhesive SEM copper tape each with a different side facing up to ensure that the thiophenol vapor could not reach the other side of the film. All spectra were further processed using Grams software. Contact angle measurements were performed with a FTA 1000 Analyze System on 1 cm² SENS. Low magnification optical images were recorded with an Olympus BX60 microscope fitted with an Olympus digital camera. For acid-treatment, a drop of concentrated nitric acid was added onto either side of a
silver SENS (aqua regia for gold SENS) with a gas chromatography syringe and observed through the optical microscope. Conventional optical images were taken with a Nikon COOLPIX L820. SEM used a Quanta FEG 250 at an acceleration voltage of 20 kV under high chamber pressure (8×10⁻⁵ mbar) with standard SEM copper tape or carbon tape as background. AFM was conducted using a Nanosurf Flex AFM in dynamic force mode. Pencil test for film hardness was conducted following standard protocols.[24] Conductivity measurements were performed with the homemade four point probe system shown in Figure. S7.

**Procedure for SENS fabrication:** Citrate-reduced silver and gold colloids were prepared via the Lee and Meisel and Turkevich-Frens methods. [31, 32] Hydroxylamine reduced silver colloid was prepared via Leopold’s method. [33] SENS were normally prepared by vigorously shaking 5 mL of aqueous NP colloid with 3 mL of polystyrene/DCM (0.05 g/mL) solution and 1.2 mL of aqueous tetrabutylammonium nitrate (10⁻⁴ mol/L) for 30 seconds. The agitated mixture was poured immediately into a polypropylene petri dish and covered with an inverted beaker. A lustrous metallic film spontaneously formed at the interface when particle-covered bubbles of DCM merged, this process took less than 1 minute. Typically, the mixture was left in air to allow all the DCM to evaporate, which created a robust polymer film with a metallic appearance at the water/air interface. The film was then separated from the walls of the petri dish with a scalpel and excess water added to float the top layer free. A piece of stiff paper was then carefully slid beneath the film to lift it from water. The film was dried in air and then peeled off from the lifting material. To reduce the evaporation time to ca. 30 minutes the beaker could be removed after the self-assembly process was complete. Larger films could be prepared by using larger volumes of the reagents in the same ratio. The large film shown in this paper was 150 mm in diameter and prepared with 300 mL of CRSC in a domestic polypropylene bowl.
Antibacterial Testing: 1 × 1 cm² sections of SENS were mounted on a rigid backing material and droplets of inoculum containing 10⁷ cfu/mL were deposited on the silver particle side, left in place for 4 hours and then removed, plated out and counted, as shown in Method S1.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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